

LIQUID CRYSTAL POLYACRYLATES

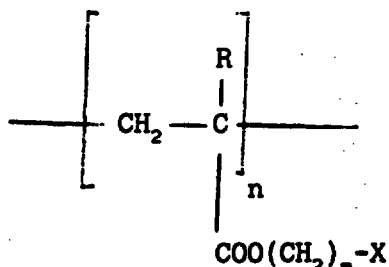
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This invention relates to a novel method for preparation of liquid crystal polyacrylates and to some novel liquid crystal polyacrylates prepared using this method.

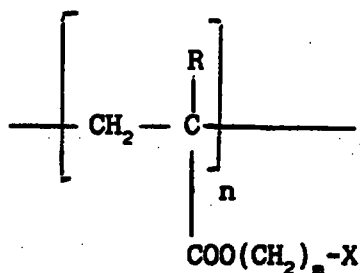
Liquid crystal polyacrylates are a generally known type of liquid crystal polymer ("LCP"). LCP's are known and are used in the electro-optical device industry, for example in optical storage devices, in non-linear optical devices and in pyroelectric devices, see for example GB 2146787 A and Makromol Chem (1985) 186 2639-47.

One known type of LCP consists of a polymeric backbone to which are attached laterally pendant side chains which have a chemical structure that is mesogenic, ie that induces liquid crystalline character, these being known as side chain liquid crystal polymers. Work in this field has identified a large number of types of side chain structures which are suitable, see for example GB 2146787 A. For some purposes it is desirable that the LCP shows a smectic C (Sc) or chiral smectic C (Sc*) liquid crystal phase, and a particularly preferred side chain for achieving this is one which contains laterally fluorinated biphenyl or terphenyl system.

In liquid crystal polyacrylates the backbone consists of a polyacrylate, eg polymethacrylate chain with pendant side chains, ie of general structure:



Where $(\text{CH}_2)_n\text{-X}$ is the side chain and R is hydrogen or alkyl in the case of polyalkylacrylates, being methyl in polymethacrylates. Such liquid crystal polyacrylates are known, eg as described in Polymer Communications (1988) 24 364-365. In Makromol. Chem. Rapid Commun. (1984) 5 393-398 chloroacrylic liquid crystal polymers are described having a general structure:

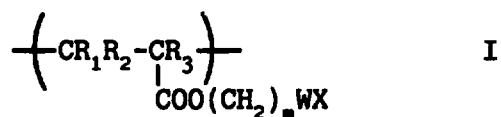


in which R is methyl or chlorine, the latter being said to favour Sc phases.

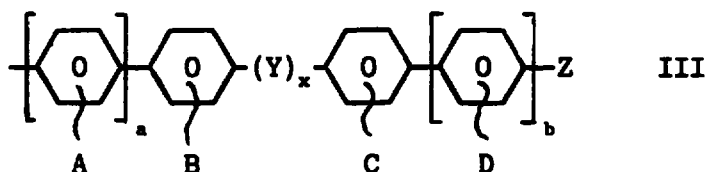
Synthesis of such liquid crystal polyacrylates has proven difficult, and there is a need for an improved method of synthesis. It is believed that these difficulties arise from the attachment of the spacer $(\text{CH}_2)_n$ into the acrylate ester monomer of the polyacrylate too early in the

synthesis, and the invention, as well as providing novel materials, seeks to alleviate these difficulties in part at least by the provision of a novel method of attachment of such a spacer group into suitable acrylate ester monomers.

According to this invention, novel liquid crystal polyacrylate homo or co-polymers having a repeat unit I are provided:



wherein R_1 and R_2 are independently alkyl or hydrogen; R_3 is alkyl, hydrogen or chlorine; m is 0 or an integer 1-20; W is a linkage group COO , OOC or O and X is a mesogenic group of formula III:



wherein a , b and x are independently 0 or 1; Y is COO , OOC , CH_2O or OCH_2 ; A , B , C and D are independently methyl, chlorine, fluorine or hydrogen and Z is cyano, halogen, $-\text{R}$, $-\text{OR}$, $-\text{OOCR}$, $-\text{COOR}$, OOCOR , or $-(\text{CO})_p\text{O}^*\text{CH}(\text{CH}_3)\text{COOR}$ where $*$ indicates an asymmetric centre and R is C_{1-15} alkyl, including alicyclic, which may itself contain an asymmetric centre which may be halogen substituted or methylated or CF_3 substituted and p is 0 or 1; when Z is OOCR then R may also be $\text{C}(\text{H})(\text{R}')\text{OR}'$ wherein R' is C_{1-5} alkyl and R' is C_{1-12} straight chain alkyl;

provided that when formula I is a homo-polymer and $W=0$, then at least one of A, B, C, D is not hydrogen;

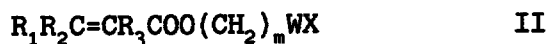
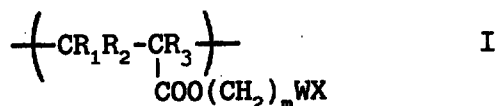
provided that when $a=0$, $B=\text{H}$, $W=0$, $x=1$, $Y=\text{CO}_2$, $C=\text{H}$, $b=1$ and $D=\text{F}$ then Z does not equal CN ;

provided that when $a=0$, $B=H$, $W=O$, $x=1$, $Y=CO_2$, $C=F$, $b=0$ then Z does not equal CN ;

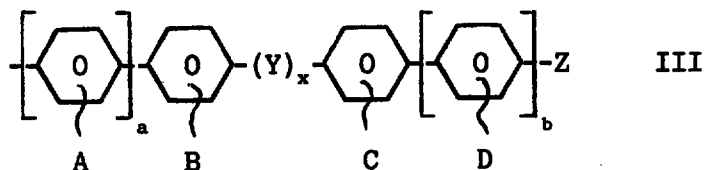
excluding terpolymers wherein $R_1=R_2=H$, $R_3 = H$ or methyl, $a=b=x=0$, $B=C=H$, $m=3-11$, $W=O$, $Z =$ methoxy, ethoxy, cyano or fluoro;

provided that when $W=COO$, $Z =$ halogen, straight chain alkyl or alkoxy, $B=C=H$, then the total of $a+b+x$ does not equal 0.

According to a further aspect of this invention a method for the preparation of a polyacrylate homo or co-polymer having a repeat unit I is provided comprising polymerisation of acrylate ester monomers of formula II with a catalyst in a solvent under irradiation or heat conditions:



wherein R_1 and R_2 are independently alkyl or hydrogen; R_3 is alkyl, hydrogen or chlorine; m is 0 or an integer 1-20; W is a linkage group COO , OOO or O and X is a mesogenic group of formula III:

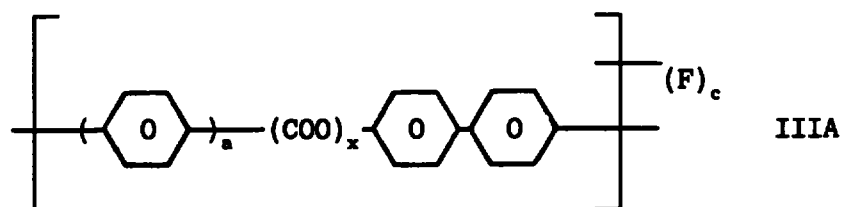


wherein a , b and x are independently 0 or 1; Y is COO , OOO , CH_2O or OCH_2 ; A , B , C and D are independently methyl, chlorine, fluorine or hydrogen and Z is cyano, halogen, $-R$, $-OR$, $-OOCR$, $-COOR$, $OOOR$, or $-(CO)_pO^*CH(CH_3)COOR$ where $*$ indicates an asymmetric centre and R is C_{1-15} alkyl, including alicyclic, which may itself contain an asymmetric centre which may be halogen substituted or methylated or CF_3 substituted and p is 0 or 1; when Z is $OOOR$ then R may also be $C(H)(R'')OR'$ wherein R'' is C_{1-5} alkyl and R' is C_{1-12} straight chain alkyl.

The preferences expressed below are with respect inter alia to ease of preparation and usefulness in preparing liquid crystal polyacrylates by polymerisation of these acrylate esters.

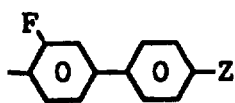
Preferably R_1 and R_2 are hydrogen. Preferably R_3 is hydrogen, chlorine or methyl. m is 0 or an integer 1-20. Preferably m is 5-15, especially 10 or 11. Lower m values are believed to result in desirable higher clearing points.

Preferred groups X for preparation of liquid crystal polyacrylates which are expected to show an S_c or S_c^* phase are fluorobiphenyl and terphenyl systems ie of general formula IIIA:

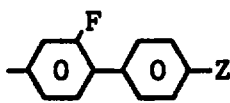


in which a and x are 0 or 1, c is 1 to 4 and the fluorine substituents may occupy any of the substitution positions on the two or three rings.

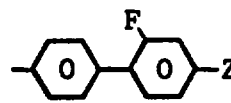
Especially preferred structures for groups of formula IIIA are listed below:



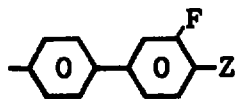
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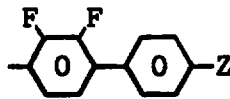
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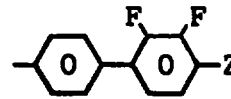
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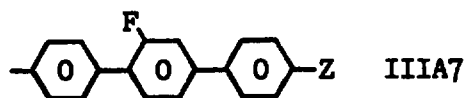
IIIA4



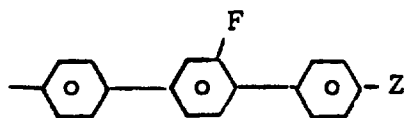
IIIA5



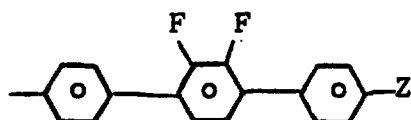
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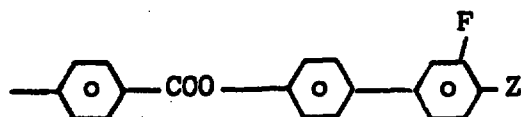
IIIA7



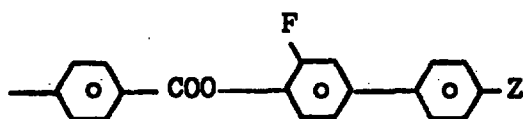
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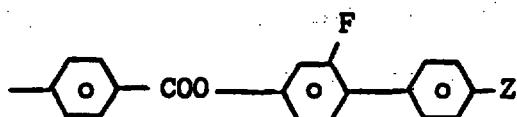
IIIA 9



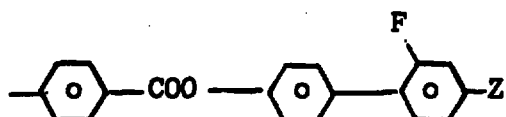
IIIA 10



IIIA 11



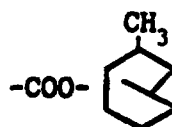
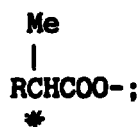
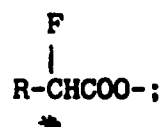
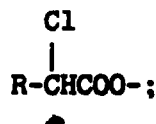
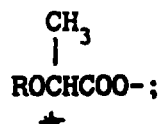
IIIA 12



IIIA 13

For the formation of Sc phases preferred groups Z in formula IIIA are C_3-C_{12} -OR where R is n-alkyl. For Sc* phases -OR or -COOR where R is asymmetrically substituted alkyl especially 2-methyl alkyl such as 2-methylheptyl, lactate ester eg $-OCH^*(CH_3)COOR$, with or without halogen

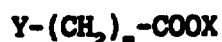
substitution such as



particularly with R as ethyl groups are preferred for Z.

The polymerization reaction may be carried out using known methods of preparing polyacrylates from acrylate ester monomers, but it is preferred to react the acrylate ester monomer with a catalyst azo-iso-butyronitrile (AIBN) in a solvent, preferably dichloroethane, toluene or especially dichloromethane, as it is believed the latter may lead to a higher molecular weight polymer product. Other free radical initiator catalysts may also be used in place of AIBN, and it may be useful to irradiate or heat the reaction mixture during the polymerization reaction.

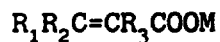
Acrylate esters of formula II above may be prepared by reacting a compound of formula IV:



IV

where Y is bromine or iodine, with an acrylic acid sodium or potassium

salt of formula:



where M is sodium or potassium.

It is preferred to carry out the reaction between the compound of formula IV and the acrylic acid salt at room temperature (ca. 20°C) in a suitable solvent, preferably hexamethyl phosphoramide (HMPA). The acrylate salt may itself be prepared by reaction of the corresponding acid $R_1R_2C=CR_3COOH$ with the metal hydride MH, eg NaH in the same solvent, hydrogen being evolved. Preferably a 1.1 : 1.0 excess of the acid to the hydride is used.

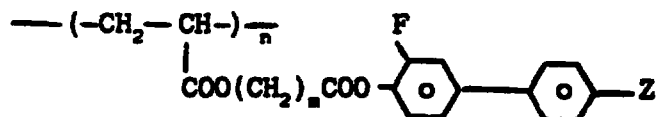
In a preliminary synthetic stage, the compound of formula IV may be prepared by esterification of a suitable phenol HO-X, with an acid of formula $Y-(CH_2)_n-COOH$, eg in a solvent such as dichloromethane using trifluoroacetic anhydride (TFAA) as a catalyst. Phenols of formula HO-X are known or may be prepared by methods apparent to those skilled in the art, for example by treatment of known phenylboronic acids with hydrogen peroxide (see M F Hawthorne J Org Chem (1957) 22 1001). Examples of methods by which such boronic acids can be prepared are given in GB 8905422A.

Acrylate esters of formula II and the polyacrylate polymer are believed to be novel. Those having a group X of formula III, in particular of formulae IIIA and the sub-variants of this IIIA 1 - IIIA 14 are expected to be of particular value in providing Sc and/or Sc* liquid crystal

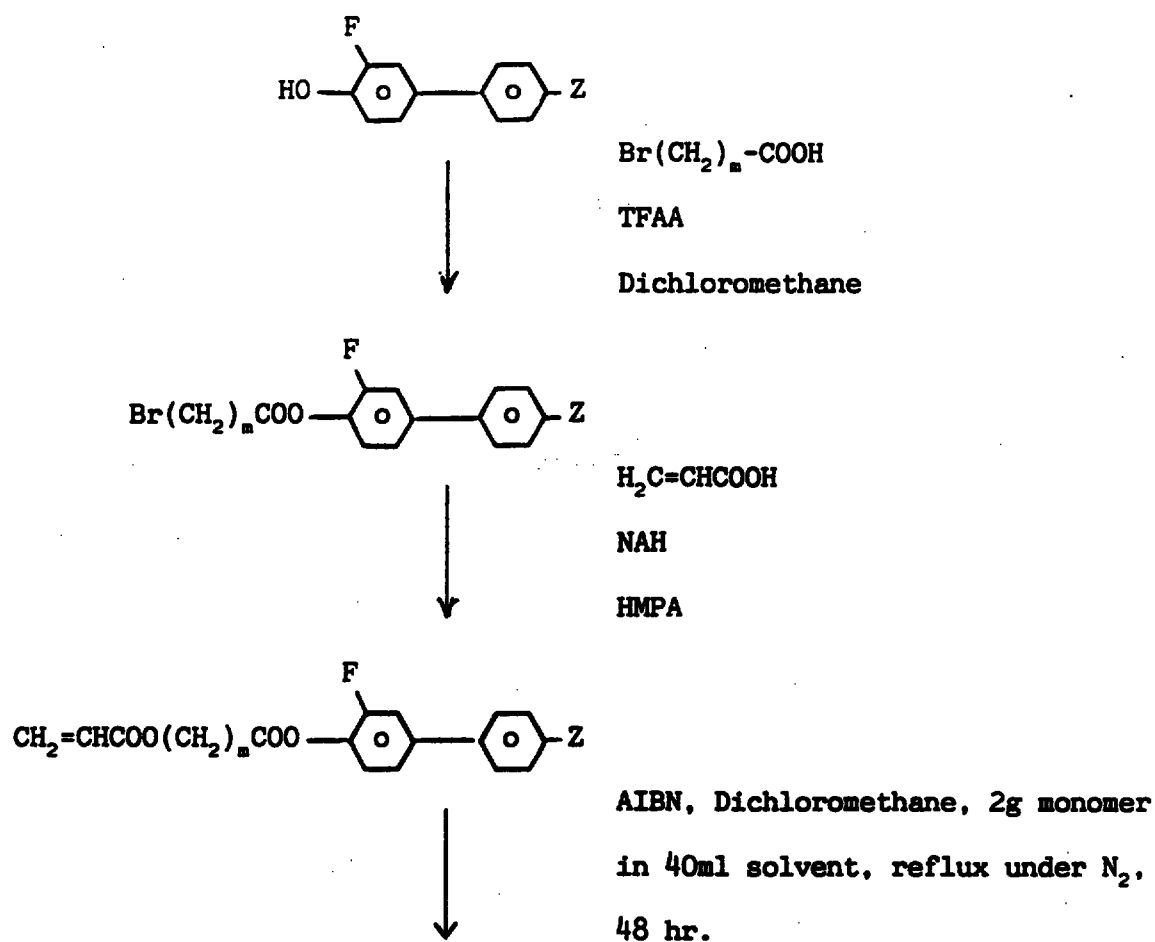
polyacrylates. In such polyacrylates those in which R_3 is chlorine might be expected to show a greater tendency to form Sc phases than their counterparts with R_3 as hydrogen or alkyl.

The invention will now be illustrated by way of non-limiting examples, with reference to Figure 1 which shows the effect of varying the spacer length m on the clearing point, ie the temperature at which the polymer becomes an isotropic liquid.

Using the method outlined above the polyacrylate polymer:



was prepared for a number of groups Z using the reactions:



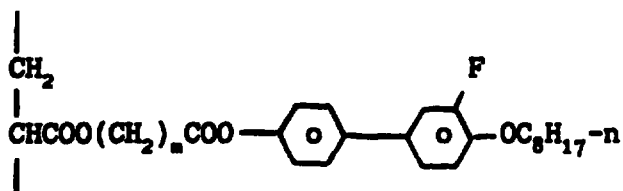
The following asymmetrically substituted fluorobiphenyl polyacrylates were synthesised. The differential scanning calorimetry (DSC) temperatures indicate phase transitions.

POLYMER	DSC TRANSITION	MICROSCOPIC
	TEMP/°C	EXAMINATION
$\begin{array}{c} \\ \text{CH}_2 \\ \\ \text{CHCOO}(\text{CH}_2)_{10}\text{COO}-\text{C}_6\text{H}_3\text{F}-\text{C}_6\text{H}_4-\text{O}2^*\text{octyl} \\ \end{array}$	2.7, 28.2	Sandy texture No phases identifiable
$\begin{array}{c} \\ \text{CH}_2 \\ \\ \text{CCH}_3\text{COO}(\text{CH}_2)_{10}\text{COO}-\text{C}_6\text{H}_3\text{F}-\text{C}_6\text{H}_4-\text{O}2^*\text{octyl} \\ \end{array}$	Tg 0.8?	No phases identifiable
$\begin{array}{c} \\ \text{CH}_2 \\ \\ \text{CCH}_3\text{COO}(\text{CH}_2)_{10}\text{COO}-\text{C}_6\text{H}_3\text{F}-\text{C}_6\text{H}_4-\text{O}^*\text{LACT} \\ \end{array}$	Tg 10.2 cp 6.3°	

2*octyl = 2-methylheptyl

*
Lact = $\text{OC}^*\text{H}(\text{CH}_3)\text{COOC}_2\text{H}_5$

To investigate the effect of pendant chain length on the transition temperatures of polymers, the following polyacrylate was synthesised with three different spacer chain lengths:

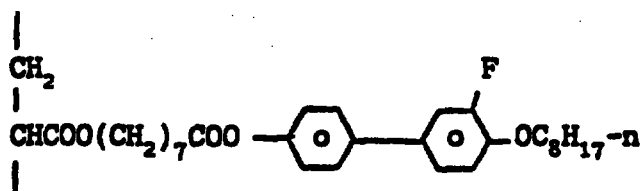


<u>m</u>	<u>DSC TRANSITION TEMP/°C</u>	<u>MICROSCOPIC EXAMINATION</u>
5	108.9, 157.4	S_A
7	46.7, 67.2, 123.7	S_A
10	47.4, 95.4, 111.9	S_A

} Focal conic texture
visible

These results show that as m increases there is a corresponding decrease in the clearing point. The effect of m on the clearing point T_{cl} is shown graphically in Fig 1.

All of the polyacrylates prepared above were polymerised using dichloroethane as solvent which tends to produce polymer chains about 9-40 repeat units long. To investigate the effect of using toluene a sample of the polymer:

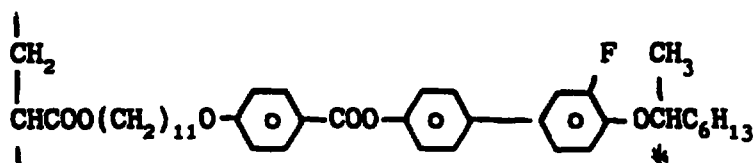
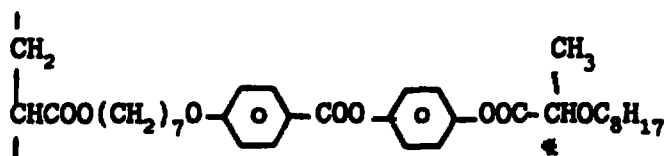
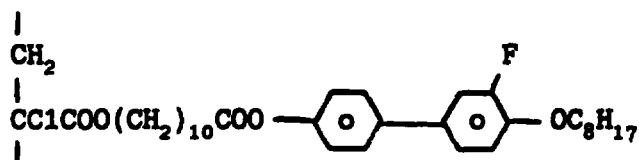
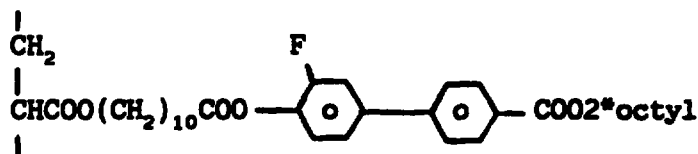
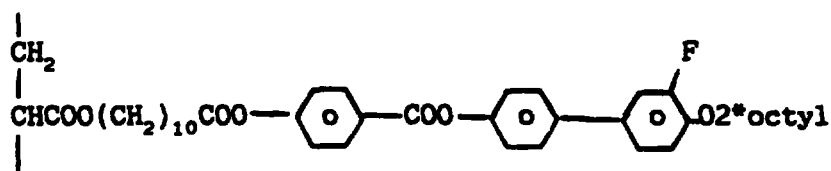
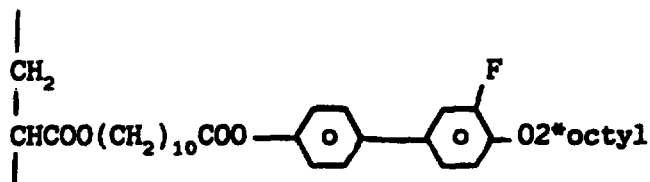


was prepared by polymerisation in dichloromethane, dichloroethane and toluene as solvents.

<u>SOLVENT</u>	<u>DSC TRANSITION TEMPS/°C</u>
Dichloroethane	46.7, 67.2, 123.7(cp)
Dichloromethane	156(cp)
Toluene	41.6, 60.6, 113.1(cp)

The transition temperatures are lower in toluene, suggesting that the two polymers differ in molecular weight.

The following polyacrylate polymers were also prepared using the method of this invention:

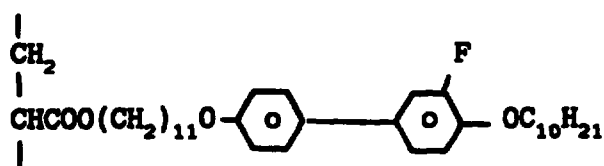


S-S 49°C

S-I 140°C

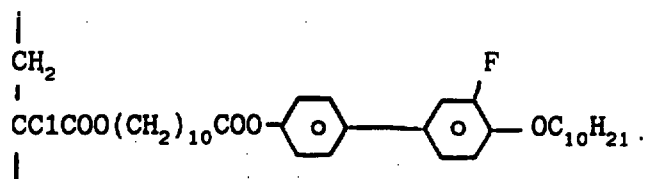
Repeat Units

= 15



S-I 88°C

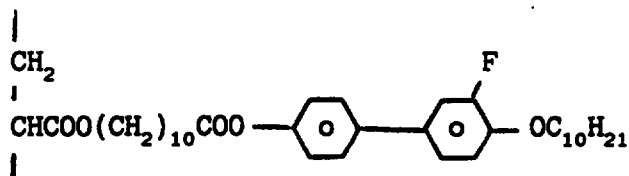
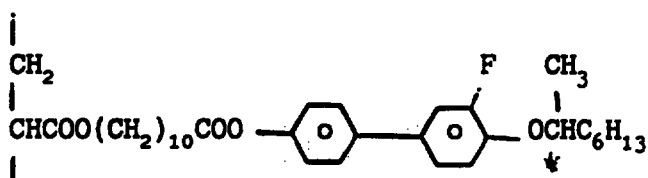
Repeat Units



S-I 139°C

Repeat Units

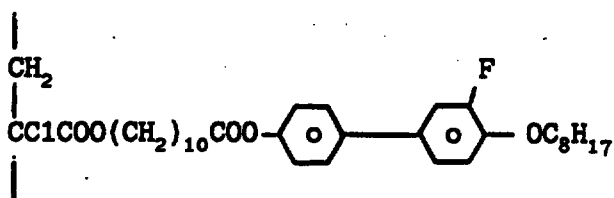
= 11

S₁-S₂ 88°CS₂-S₃ 117°CS₃-SI 147°C

S-I 61°C

Repeat Units

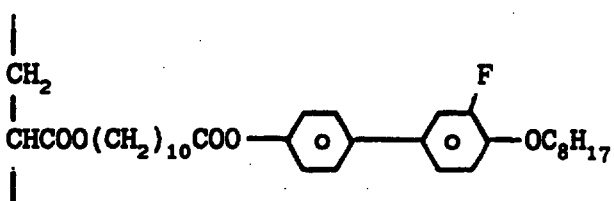
= 11



Sc-I 137°C

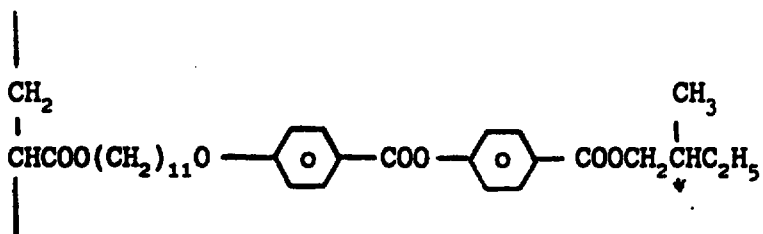
Repeat Units

= 37

S_I-Sc 47°CSc-S_A 95°CS_A-I 112°C

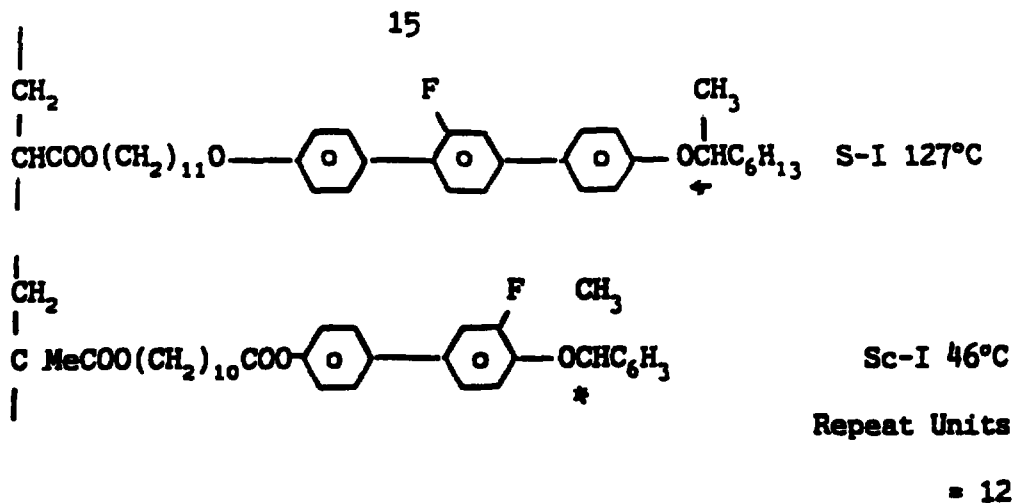
Repeat Units

= 10

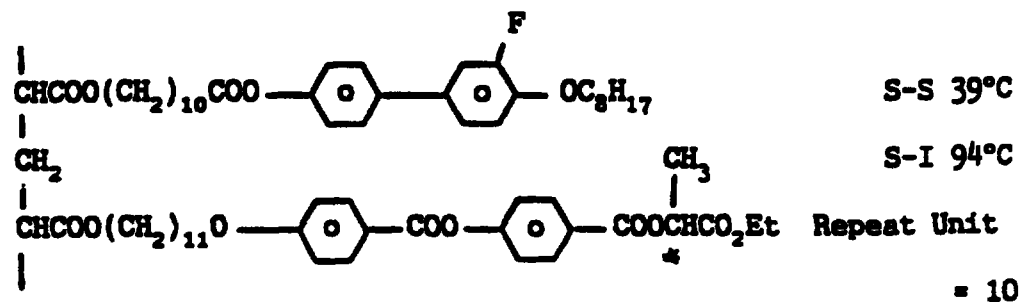
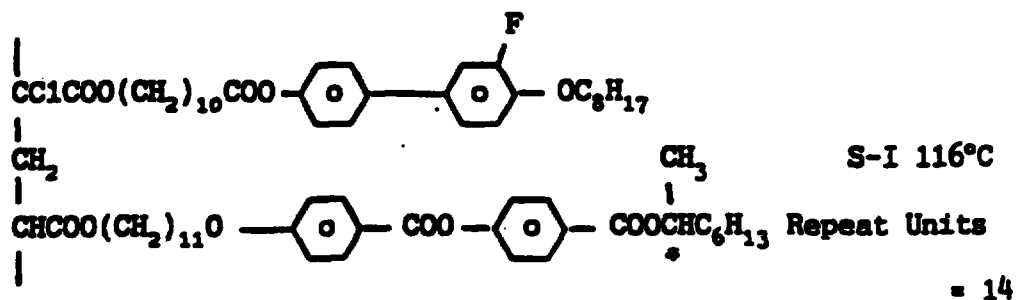


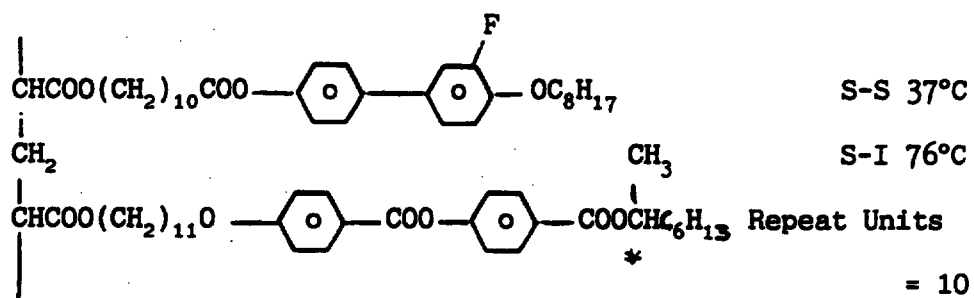
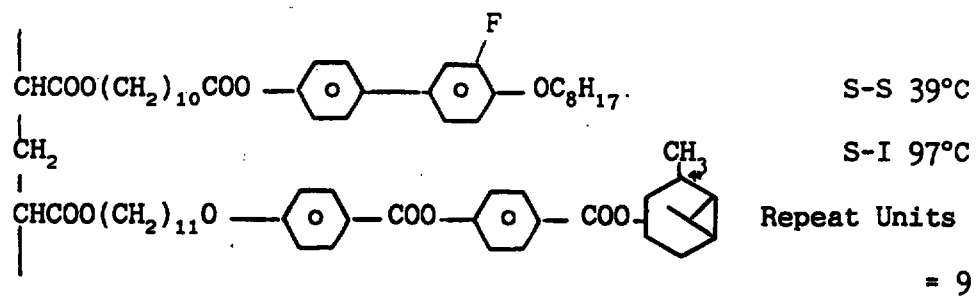
Tg - 7

S-I 84°C



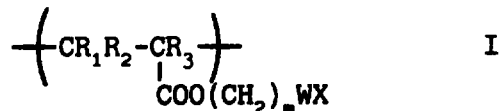
The following polyacrylate copolymers were also prepared using the method of this invention.



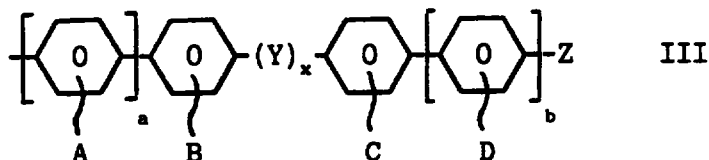


CLAIMS

1. A liquid crystal polyacrylate homo or co-polymer having a repeat unit I:



wherein R_1 and R_2 are independently alkyl or hydrogen; R_3 is alkyl, hydrogen or chlorine; m is 0 or an integer 1-20; W is a linkage group COO , OOC or O and X is a mesogenic group of formula III:



wherein a , b and x are independently 0 or 1; Y is COO , OOC , CH_2O or OCH_2 ; A , B , C and D are independently methyl, chlorine, fluorine or hydrogen and Z is cyano, halogen, $-\text{R}$, $-\text{OR}$, $-\text{OOCR}$, $-\text{COOR}$, OOCOR , or $-(\text{CO})_p\text{O}^*\text{CH}(\text{CH}_3)\text{COOR}$ where $*$ indicates an asymmetric centre and R is C_{1-15} alkyl, including alicyclic, which may itself contain an asymmetric centre which may be halogen substituted or methylated or CF_3 substituted and p is 0 or 1; when Z is OOCR then R may also be $\text{C}(\text{H})(\text{R}')\text{OR}'$ wherein R' is C_{1-5} alkyl and R is C_{1-12} straight chain alkyl;

provided that when formula I is a homo-polymer and $W=\text{O}$, then at least one of A, B, C, D is not hydrogen;

provided that when $a=0$, $B=\text{H}$, $W=\text{O}$, $x=1$, $Y=\text{CO}_2$, $C=\text{H}$, $b=1$ and $D=\text{F}$ then Z does not equal CN ;

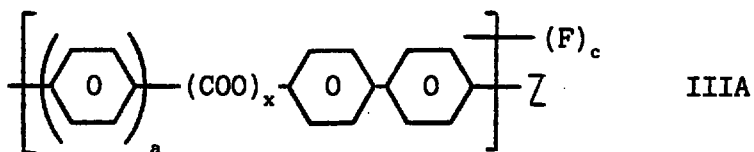
provided that when $a=0$, $B=\text{H}$, $W=\text{O}$, $x=1$, $Y=\text{CO}_2$, $C=\text{F}$, $b=0$ then Z does not equal CN ;

excluding terpolymers wherein $\text{R}_1=\text{R}_2=\text{H}$, $\text{R}_3 = \text{H}$ or methyl, $a=b=x=0$, $B=C=\text{H}$, $m=3-11$, $W=\text{O}$, $Z = \text{methoxy, ethoxy, cyano or fluoro}$;



provided that when $W=COO$, Z = halogen, straight chain alkyl or alkoxy, $B=C=H$, then the total of $a+b+x$ does not equal 0.

2. A liquid crystal polyacrylate polymer according to claim 1 in which the mesogenic group X is a fluorobiphenyl or terphenyl system of general formula IIIA:

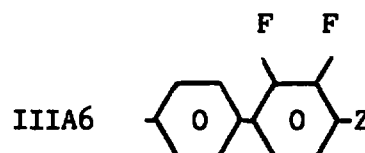
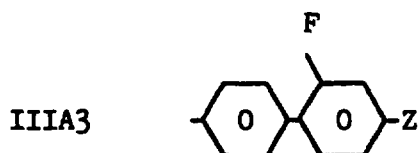
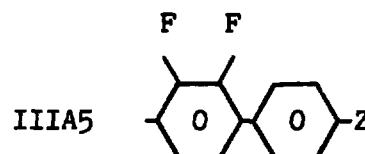
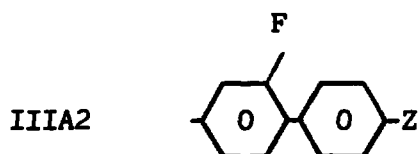
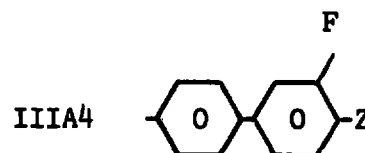
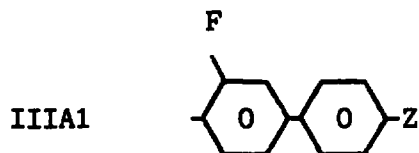


wherein a and x are 0 or 1, c is 1 to 4 and the fluorine substituents may occupy any of the substitution positions on the two or three rings;

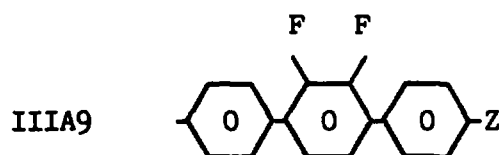
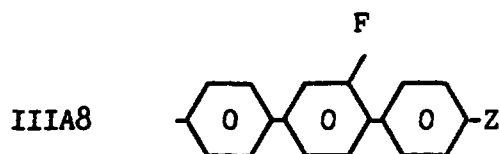
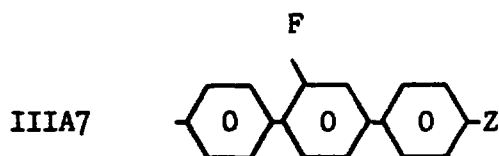
provided that if $a=0$ then $x=0$.



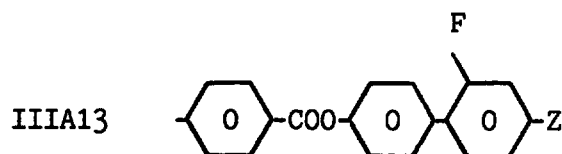
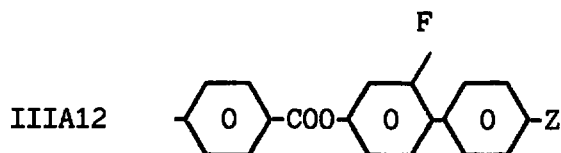
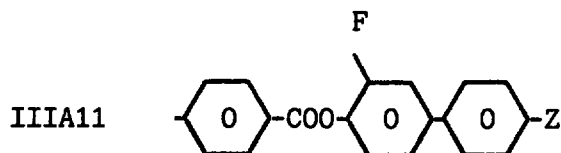
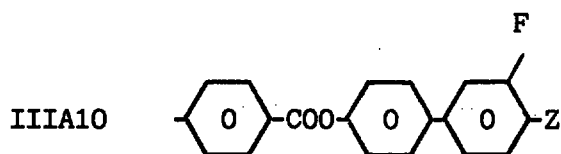
3. A liquid crystal polyacrylate polymer according to claim 2 in which the particularly preferred mesogenic group X is of formula IIIA1 to IIIA6:



4. A liquid crystal polyacrylate polymer according to claim 2, in which the particularly preferred mesogenic group X is of formula IIIA7 to IIIA9:



5. A liquid crystal polyacrylate polymer according to claim 2 in which the particularly preferred mesogenic group X is of formula IIIA10 to IIIA13:

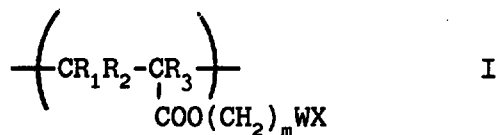


6. A liquid crystal polyacrylate polymer according to claim 2 in which the preferred Z groups are C_{3-12} -OR where R is n-alkyl; -OR or COOR where R is asymmetrically substituted alkyl especially 2-methyl alkyl such as 2-methylheptyl; lactate ester such as $-OCH(CH_3)COOR$ with or without halogen substitution such as $-RCH(CF_3)COO-$, $ROCH(CF_3)COO-$, $ROCH(CH_3)COO$, $RCH(Cl)COO-$, $RCH(F)COO$, $RCH(Me)COO-$,

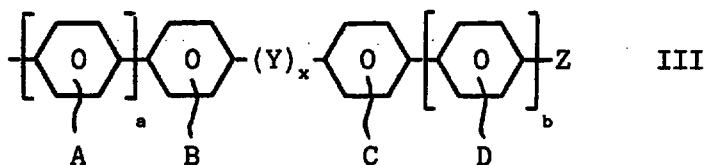
R-COO-  , particularly preferred is R as ethyl groups.



7. A method of preparing liquid crystal polyacrylate polymers of the following formulae comprising polymerisation of acrylate ester monomers with a catalyst in a solvent under irradiation or heat conditions



wherein R_1 and R_2 are independently alkyl or hydrogen; R_3 is alkyl, hydrogen or chlorine; m is 0 or an integer 1-20; W is a linkage group COO , OOC or O and X is a mesogenic group of formula III:



wherein a , b and x are independently 0 or 1; Y is COO , OOC , CH_2O or OCH_2 ; A , B , C and D are independently methyl, chlorine, fluorine or hydrogen and Z is cyano, halogen, $-\text{R}$, $-\text{OR}$, $-\text{OOCR}$, $-\text{COOR}$, OOCOR , or $-(\text{CO})_p\text{O}^*\text{CH}(\text{CH}_3)\text{COOR}$ where $*$ indicates an asymmetric centre and R is C_{1-15} alkyl including alicyclic which may itself contain an asymmetric centre which may be halogen substituted or methylated or CF_3 substituted and p is 0 or 1; when Z is OOCR then R may also be $\text{C}(\text{H})(\text{R}')\text{OR}'$ wherein R' is C_{1-5} alkyl and R is C_{1-12} straight chain alkyl.



8. A method according to claim 7, in which the catalyst is azo-iso-butyronitrile.
 9. A method according to claim 8, in which the catalyst is another free radical initiator.
 10. A method according to claim 7, in which the solvent is dichloromethane.
 11. A method according to claim 10 in which the solvent is toluene or dichloroethane.
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